

CELLS FOR THE ELECTROWINNING OF ALUMINIUM HAVING
DIMENSIONALLY STABLE METAL-BASED ANODES

Field of the Invention

This invention relates to cells for the electrowinning of aluminium by the electrolysis of alumina dissolved in a molten fluoride-containing electrolyte provided with dimensionally stable oxygen-evolving anodes, and to methods for the fabrication and reconditioning of such anodes, as well as to the operation of such cells to maintain the anodes dimensionally stable.

Background Art

The technology for the production of aluminium by the electrolysis of alumina, dissolved in molten cryolite, at temperatures around 950°C is more than one hundred years old.

This process, conceived almost simultaneously by Hall and Héroult, has not evolved as many other electrochemical processes.

The anodes are still made of carbonaceous material and must be replaced every few weeks. The operating temperature is still not less than 950°C in order to have a sufficiently high solubility and rate of dissolution of alumina and high electrical conductivity of the bath.

The carbon anodes have a very short life because during electrolysis the oxygen which should evolve on the anode surface combines with the carbon to form polluting CO₂ and small amounts of CO and fluorine-containing dangerous gases. The actual consumption of the anode is as much as 450 Kg/Ton of aluminium produced which is more than 1/3 higher than the theoretical amount of 333 Kg/Ton.

The frequent substitution of the anodes in the cells is still a clumsy and unpleasant operation. This cannot be avoided or greatly improved due to the size and weight of the anode and the high temperature of operation.

5 Several improvements were made in order to increase the lifetime of the anodes of aluminium electrowinning cells, usually by improving their resistance to chemical attacks by the cell environment and air to those parts of the anodes which remain outside the bath. However, most
10 attempts to increase the chemical resistance of anodes were coupled with a degradation of their electrical conductivity.

US Patent 4,614,569 (Duruz et al.) describes anodes for aluminium electrowinning coated with a protective
15 coating of cerium oxyfluoride, formed in-situ in the cell or pre-applied, this coating being maintained by the addition of cerium to the molten cryolite electrolyte. This made it possible to have a protection of the surface only from the electrolyte attack and to a certain extent
20 from the gaseous oxygen but not from the nascent monoatomic oxygen.

EP Patent application 0 306 100 (Nyguen/Lazouni/Doan) describes anodes composed of a chromium, nickel, cobalt and/or iron based substrate covered with an oxygen
25 barrier layer and a ceramic coating of nickel, copper and/or manganese oxide which may be further covered with an in-situ formed protective cerium oxyfluoride layer.

Likewise, US Patents 5,069,771, 4,960,494 and 4,956,068✓ (all Nyguen/Lazouni/Doan) disclose aluminium
30 production anodes with an oxidised copper-nickel surface on an alloy substrate with a protective barrier layer. However, full protection of the alloy substrate was difficult to achieve.

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A significant improvement described in US Patent 5,510,008, and in International Application WO96/12833 (Sekhar/Liu/Duruz) involved micropyrethically producing a body from nickel, aluminium, iron and copper and oxidising the surface before use or in-situ. By said micropyrethic methods materials have been obtained whose surfaces, when oxidised, are active for the anodic reaction and whose metallic interior has low electrical resistivity to carry a current from high electrical resistant surface to the busbars. However it would be useful, if it were possible, to simplify the manufacturing process of these materials and increase their life to make their use economic.

US Patent 4,999,097 (Sadoway) describes anodes for conventional aluminium electrowinning cells provided with an oxide coating containing at least one oxide of zirconium, hafnium, thorium and uranium. To prevent consumption of the anode, the bath is saturated with the materials that form the coating. However, these coatings are poorly conductive and have not found commercial acceptance.

US Patent 4,504,369 (Keller) discloses a method for producing aluminium in a conventional cell using anodes whose dissolution into the electrolytic bath is reduced by adding anode constituent materials into the electrolyte, allowing slow dissolution of the anode. However, this method is impractical because it would lead to a contamination of the product aluminium by the anode constituent materials which is considerably above the acceptable level in industrial production. To limit contamination of the product aluminium, it was suggested to reduce the reduction rate of the dissolved constituent materials at the cathode, by limiting the cathode surface area or by reducing mass transfer rates by other means. However, the feasibility of these proposals has never been demonstrated, nor was it contemplated that the amount of the anode constituent materials dissolved in the electrolyte should be reduced.

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US Patent 4,614,569 (Duruz et al) describes metal anodes for aluminium electrowinning coated with a protective coating of cerium oxyfluoride, formed in-situ in the cell or pre-applied, this coating being maintained by the addition of small amounts of cerium to the molten cryolite electrolyte so as to protect the surface of the anode from the electrolyte attack. All other attempts to reduce the anode wear by slowing dissolution of the anode with an adequate concentration of its constituents in the molten electrolyte, for example as described in US Patents 4,999,097 (Sadoway) and 4,504,369 (Keller), have failed.

In known processes, even the least soluble anode material releases excessive amounts constituents into the bath, which leads to an excessive contamination of the product aluminium. For example, the concentration of nickel (a frequent component of stable anodes) found in aluminium produced in laboratory tests at conventional cell operating temperatures is typically comprised between 800 and 2000 ppm, i.e. 4 to 10 times the acceptable level which is 200 ppm.

The extensive research which was carried out to develop suitable metal anodes having limited dissolution did not find any commercial acceptance because of the excessive contamination of the product aluminium by the anode materials.

Objects of the Invention

A major object of the invention is to provide an anode for aluminium electrowinning of which has no carbon so as to eliminate carbon-generated pollution and increase the anode life.

A further object of the invention is to provide an aluminium electrowinning anode material with a surface having a high electrochemical activity for the oxidation

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of oxygen ions for the formation of bimolecular gaseous oxygen and a low solubility in the electrolyte.

5 An important object of the invention is to reduce the solubility of the surface layer of an aluminium electrowinning anode, thereby maintaining the anode dimensionally stable without excessively contaminating the product aluminium.

10 Another object of the invention is to provide operating conditions for an aluminium electrowinning cell under which conditions the contamination of the product aluminium is limited.

15 A subsidiary object of the invention is to provide a cell for the electrowinning of aluminium whose side walls are resistant to electrolyte, thereby allowing operation of the cell without formation of a frozen electrolyte layer on the side walls and with reduced thermal loss.

Summary of the Invention

20 The invention is based on the observation that iron oxides and in particular hematite (Fe_2O_3) have a higher solubility than nickel in molten electrolyte. However, in industrial production the contamination tolerance of the product aluminium by iron oxides is also much higher (1000 to 2000 ppm) than for other metal
25 impurities.

Solubility is an intrinsic property of anode materials and cannot be changed otherwise than by modifying the electrolyte composition or the operative temperature of a cell.

30 Laboratory scale cell tests utilising a $\text{NiFe}_2\text{O}_4/\text{Cu}$ cermet anode and operating under steady state were carried out to establish the concentration of iron in molten

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electrolyte and in the product aluminium under different operating conditions.

In the case of iron oxide, it has been observed that lowering the temperature of the electrolyte lowers of the limit of solubility of iron species. This effect can surprisingly be exploited to produce a major impact on cell operation by limiting the contamination of the product aluminium by iron.

Thus, it has been found that when the temperature of the cell is reduced below the temperature of conventional cells an anode coated with an outer layer of iron oxide can be made dimensionally stable by maintaining a concentration of iron species in the molten electrolyte sufficient to suppress the dissolution of the anode coating but low enough not to exceed the industrial acceptable level of iron in the product aluminium.

Cells and Operation

The invention provides a cell for the electrowinning of aluminium by the electrolysis of alumina dissolved in a molten fluoride-containing electrolyte. The cell comprises one or more anodes, each having a metal-based substrate and an electrochemically-active iron oxide-based outside layer, in particular a hematite-based layer, which remains dimensionally stable by maintaining in the electrolyte a sufficient concentration of iron species. The cell operating temperature is sufficiently low so that the required concentration of iron species in the electrolyte is limited by the reduced solubility of iron species in the electrolyte at the operating temperature, which consequently limits the contamination of the product aluminium by iron to an acceptable level.

In the context of this invention:

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- a metal-based anode means that the anode contains at least one metal in the anode substrate as such or as an alloy, intermetallic and/or cermet.

5 - an iron oxide-based layer means that the layer contains predominately iron oxide, as a simple oxide such as hematite, or as part of an electrically conductive and electrochemically active double or multiple oxide, such as a ferrite, in particular cobalt, manganese, nickel, magnesium or zinc ferrite.

10 More generally, the iron-oxide may be present in the electrochemically active layer as such, in a multi-compound mixed oxide, in mixed crystals and/or in a solid solution of oxides, in the form of a stoichiometric or non-stoichiometric oxide.

15 The solubility of iron species in the electrolyte may be influenced by the presence in the electrolyte of species other than iron, such as aluminium, calcium, lithium, magnesium, nickel, sodium, potassium and/or barium species.

20 Usually, the iron oxide-based outside layer of the anode is either an applied layer or obtainable by oxidising the surface of the anode substrate which contains iron as further described below.

25 The cell is usually operated with an operating temperature of the electrolyte below 910°C. The operating temperature of the electrolyte is usually above 700°C, and preferably between 800°C and 850°C.

30 The electrolyte may contain NaF and AlF₃ in a molar ratio NaF/AlF₃ comprised between 1.2 and 2.4. The concentration of alumina dissolved in the electrolyte is usually below 10 weight%, usually between 2 weight% and 8 weight%.

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In order for the produced aluminium to be commercially acceptable, the amount of dissolved iron in the electrolyte which prevents dissolution of the iron oxide-based anode layer is such that the product aluminium is contaminated by no more than 2000 ppm iron, preferably by no more than 1000 ppm iron, and if required by no more than 500 ppm iron.

The cell may comprise means for periodically or intermittently feeding iron species into the electrolyte to maintain the required amount of iron species in the electrolyte at the operating temperature which prevents the dissolution of the iron oxide-based anode layer. The means for feeding iron species may feed iron metal and/or an iron compound, such as iron oxide, iron fluoride, iron oxyfluoride and/or an iron-aluminium alloy.

The means for feeding iron species may periodically feed iron species together with alumina into the electrolyte. Alternatively, the means for feeding iron species may be a sacrificial electrode continuously feeding iron species into the electrolyte.

Advantageously, the cell may comprise at least one aluminium-wettable cathode which can be a drained cathode on which aluminium is produced and from which it continuously drains.

Usually, the cell is in a monopolar, multi-monopolar or in a bipolar configuration. Bipolar cells may comprise the anodes as described above as the anodic side of at least one bipolar electrode and/or as a terminal anode.

In such a bipolar cell an electric current is passed from the surface of the terminal cathode to the surface of the terminal anode as ionic current in the electrolyte and as electronic current through the bipolar electrodes, thereby electrolysing the alumina dissolved in

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the electrolyte to produce aluminium on each cathode surface and oxygen on each anode surface.

Preferably, the cell comprises means to improve the circulation of the electrolyte between the anodes and facing cathodes and/or means to facilitate dissolution of alumina in the electrolyte. Such means can for instance be provided by the geometry of the cell as described in co-pending application PCT/IB98/00161 (de Nora/Duruz) or by periodically moving the anodes as described in co-pending application PCT/IB98/00162 (Duruz/Bellò).

The cell according to the invention may also have side walls provided with a iron oxide-based outside layer which is during cell operation in contact only with the electrolyte and which is maintained dimensionally stable by the amount of iron species dissolved in the electrolyte. The iron oxide-based layer on the side walls may be in contact with molten electrolyte. By maintaining the side walls free from frozen electrolyte, the cell may be operated with reduced thermal loss.

The invention relates also to a method of producing aluminium in a cell as described hereabove. The method comprises keeping the anode dimensionally stable during electrolysis by maintaining a sufficient concentration of iron species in the electrolyte, and operating the cell at a sufficiently low temperature so that the required concentration of iron species in the electrolyte is limited by the reduced solubility of iron species in the electrolyte at the operating temperature, which consequently limits the contamination of the product aluminium by iron to an acceptable level.

Cell Components and Methods of Fabrication

Another aspect of the invention is an anode which can be maintained dimensionally stable in a cell as described above. The anode has a metal-based substrate

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comprising at least one metal, an alloy, an intermetallic compound or a cermet. The substrate is covered with an iron oxide-based outside layer, in particular a hematite-based layer, which is electrochemically active for the oxidation of oxygen ions into molecular oxygen.

As already stated above, the iron oxide-based outside layer of the anode is usually either an applied layer or obtainable by oxidising the surface of the anode substrate which contains iron.

The iron oxide-based layer may be in-situ electro-deposited on the anode substrate.

Alternatively, the iron oxide-based layer may be applied as a colloidal and/or polymeric slurry, and dried and/or heat treated. The colloidal and/or polymeric slurry may comprise at least one of alumina, ceria, lithia, magnesia, silica, thoria, yttria, zirconia, tin oxide and zinc oxide.

The iron oxide-based layer may also be formed by plasma spraying iron oxide or iron onto the anode substrate followed by an oxidation treatment.

The iron oxide-based layer may be formed, or consolidated, by heat treating an anode substrate, the surface of which contains iron and/or iron oxide, in an oxidising gas at a temperature which is at least 50°C above the operative temperature of the cell in which the anode is to be inserted for a period of at least 1 hour.

Usually, the anode substrate is heat treated in air or in oxygen at a temperature of 950°C to 1300°C, preferably at a temperature of 1050°C to 1200°C. The anode substrate may be heat treated for a period of 2 to 10 hours at a temperature above 1150°C or for a period of at least 6 hours when the temperature is below 1050°C.

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The iron oxide-based layer can comprise a dense iron oxide outer portion, a microporous intermediate iron oxide portion and an inner portion containing iron oxide and a metal from the surface of the anode substrate.

5 The anode substrate may comprise a plurality of layers carrying on the outermost layer the iron oxide-based layer. For instance, the anode substrate may be made by forming on a core layer an oxygen barrier layer which is coated with at least one intermediate layer carrying
10 the iron oxide-based layer, the oxygen barrier layer being formed before or after application of the intermediate layer(s).

15 The oxygen barrier layer may be formed by applying a coating onto the core layer before application of the intermediate layer(s) or by surface oxidation of the core layer before or after application of the intermediate layer(s).

20 The oxygen barrier layer and/or the intermediate layer may be formed by slurry application of a precursor. Alternatively, the oxygen barrier layer and/or the intermediate layer may be formed by plasma spraying oxides thereof, or by plasma spraying metals and forming the oxides by heat treatment.

25 Usually, the oxygen barrier layer contains chromium oxide and/or black non-stoichiometric nickel oxide which is covered with an intermediate layer containing copper, or copper and nickel, and/or their oxides.

30 A preferred embodiment of the anode is a composite, high-temperature resistant, non-carbon, metal-based anode having a metal-based core structure of low electrical resistance for connecting the anode to a positive current supply and coated with a series of

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superimposed, adherent, electrically conductive layers consisting of:

- a) at least one layer on the metal-based core structure forming a barrier substantially impervious to monoatomic oxygen;
- b) one or more intermediate layers on the outermost oxygen barrier layer to protect the oxygen barrier and which remain inactive in the reactions for the evolution of oxygen gas and inhibit the dissolution of the oxygen barrier; and
- c) an electrochemically-active iron oxide-based outside layer, in particular a hematite-based layer, on the outermost intermediate layer, for the oxidation reaction of oxygen ions present at the anode/electrolyte interface into monoatomic oxygen, as well as for subsequent reaction for the formation of biatomic molecular oxygen evolving as gas.

In some embodiments, the iron oxide layer is coated onto a passivable and inert anode substrate.

Different types of anode substrate may be used to carry an applied iron oxide-based layer. Usually, the anode substrate comprises at least one metal, an alloy, an intermetallic compound or a cermet.

The anode substrate may for instance comprise at least one of nickel, copper, cobalt, chromium, molybdenum, tantalum, iron, and their alloys or intermetallic compounds, and combinations thereof. For instance, the anode substrate may comprise an alloy consisting of 10 to 30 weight% of chromium, 55 to 90% of at least one of nickel, cobalt or iron, and 0 to 15% of aluminium, titanium, zirconium, yttrium, hafnium or niobium.

Alternatively, some iron-containing anode substrates are suitable for carrying a iron oxide-based

layer which is either applied onto the surface of the anode substrate or obtained by oxidation of the surface of the substrate. The anode substrate may for instance contain an alloy of iron and at least one alloying metal selected from nickel, cobalt, molybdenum, tantalum, niobium, titanium, zirconium, manganese and copper, in particular between 50 and 80 weight% iron and between 20 and 50 weight% nickel, preferably between 60 and 70 weight% iron and between 30 and 40 weight% nickel.

Another aspect of the invention is a bipolar electrode which comprises on its anodic side an anode as described above and which can be maintained dimensionally stable during operation in a bipolar cell.

These anode materials may also be used to manufacture cell sidewalls which can be maintained dimensionally stable during operation of the cell as described above.

A further aspect of the invention is a cell component which can be maintained dimensionally stable in a cell as described above, having an iron oxide-based outside layer, in particular a hematite-based layer, which is electrochemically active for the oxidation of oxygen ions into molecular oxygen. The hematite-based layer may cover a metal-based anode substrate comprising at least one metal, an alloy, an intermetallic compound or a cermet.

Yet another aspect of the invention is a method of manufacturing an anode of a cell as described above. The method comprises forming an iron oxide-based outside layer on a metal-based anode substrate made of at least one metal, an alloy, an intermetallic compound or a cermet either by oxidising the surface of the anode substrate which contains iron, or by coating the iron oxide-based layer onto the substrate.

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This method may also be used for reconditioning an anode as described above, whose iron oxide-based layer is damaged. The method comprises clearing at least the damaged parts of the iron oxide-based layer from the anode substrate and then reconstituting at least the iron oxide-based layer.

Brief Description of the Drawings

The invention will now be described by way of example with reference to the accompanying schematic drawings, in which:

- Figure 1 is a cross-sectional view through an anode made of an anode substrate comprising a plurality of layers and carrying on the outermost layer the iron oxide-based layer, and

- Figure 1a is a magnified view of a modification of the applied layers of the anode of Figure 1.

Detailed Description

Figure 1 shows an anode 10 according to the invention which is immersed in an electrolyte 5. The anode 10 contains a layered substrate comprising a core 11 which may be copper, an intermediate layer 12, such as electrodeposited nickel, covering the core 11, to provide an anchorage for an oxygen barrier layer 13. The oxygen barrier 13 may be applied by electrodepositing a metal such as chromium and/or nickel and heat treating in an oxidising media to form chromium oxide and/or black non-stoichiometric nickel oxide.

On the oxygen barrier layer 13 is a protective intermediate layer 14 which can be obtained by electrodepositing or plasma spraying and then oxidising either a nickel-copper alloy layer, or a nickel layer and

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a copper layer and interdiffusing the applied nickel and copper layers before oxidation. The protective intermediate layer 14 protects the oxygen barrier layer 13 by inhibiting its dissolution.

5 The protective intermediate layer 14 is covered with an electrodeposited or plasma-sprayed iron layer 15 which is surface oxidised to form an electrochemically active hematite-based surface layer 16, forming the outer surface of the anode 10 according to the invention.

10 In Figure 1, the iron layer 15 and the electrochemically active hematite-based surface layer 16 cover the substrate of the anode 10 where exposed to the electrolyte 5. However the iron layer 15 and the hematite-based layer 16 may extend far above the surface of the
15 electrolyte 5, up to the connection with a positive current bus bar.

 Figure 1a shows a magnified view of a modification of the applied layers of the anode 10 of Figure 1. Instead of a single intermediate layer 14 shown in Figure 1, the
20 anode 10 as shown in Figure 1a comprises two distinct intermediate protective layers 14A,14B.

 Similarly to the anode 10 of Figure 1, the anode 10 of Figure 1a comprises a core 11 which may be copper covered with a nickel plated layer 12 forming an anchorage
25 for a chromium oxide oxygen barrier layer 13. However, the single oxidised interdiffused or alloyed nickel copper layer 14 shown in Figure 1 is modified in Figure 1a by firstly applying on the oxygen barrier 13 a nickel layer 14A followed by a copper layer 14B. The nickel and copper
30 layers 14A,14B are oxidised at 1000°C in air without prior interdiffusion by a heat treatment in an inert atmosphere, thereby converting these layers into a nickel oxide rich layer 14A and a copper oxide rich layer 14B. The nickel oxide rich layer 14A and the copper oxide rich layer 14B
35 may interdiffuse during use in the cell.

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The intermediate layers 14,14A,14B may either be oxidised before use of the anode 10, before or after application of an iron layer 15, or during normal electrolysis in a cell.

5 The intermediate layers 14A,14B of the anode 10 of Figure 1a are covered with an electrodeposited or plasma-sprayed iron layer 15 which is surface oxidised to form an electrochemically active hematite-based surface layer 16, forming the outer surface of the anode 10 according to the
10 invention.

The invention will be further described in the following Examples:

Example 1

Aluminium was produced in a laboratory scale cell
15 comprising an anode according to the invention.

The anode was made by pre-oxidising in air at about 1100°C for 10 hours a substrate of a nickel-iron alloy consisting of 30 weight% nickel and 70 weight% iron, thereby forming a dense hematite-based surface layer on
20 the alloy.

The anode was then tested in a fluoride-containing molten electrolyte at 850°C containing NaF and AlF_3 in a molar ratio NaF/ AlF_3 of 1.9 and approximately 6 weight% alumina at a current density of about 0.8 A/cm².
25 Furthermore, the electrolyte contained approximately 180 ppm iron species obtained from the dissolution of iron oxide thereby saturating the electrolyte with iron species and inhibiting dissolution of the hematite-based anode surface layer.

30 To maintain the concentration of dissolved alumina in the electrolyte, fresh alumina was periodically fed into the cell. The alumina feed contained sufficient iron oxide so as to replace the iron which had deposited into

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the product aluminium, thereby maintaining the concentration of iron in the electrolyte at the limit of solubility and preventing dissolution of the hematite-based anode surface layer.

5 The anode was extracted from the electrolyte after 100 hours and showed no sign of significant internal or external corrosion after microscopic examination of a cross-section of the anode specimen.

10 The produced aluminium was also analysed and showed an iron contamination of about 800 ppm which is below the tolerated iron contamination in commercial aluminium production.

Example 2

15 An anode was made by coating by electro-deposition a structure in the form of an rod having a diameter of 12 mm consisting of 74 weight% nickel, 17 weight% chromium and 9 weight% iron, such as Inconel®, first with a nickel layer about 200 micron thick and then a copper layer about 100 micron thick.

20 The coated structure was heat treated at 1000°C in argon for 5 hours. This heat treatment provides for the interdiffusion of nickel and copper to form an intermediate layer. The structure was then heat treated for 24 hours at 1000°C in air to form a chromium oxide
25 barrier layer on the core structure and oxidising at least partly the interdiffused nickel-copper layer thereby forming the intermediate layer.

30 A further layer of a nickel-iron alloy consisting of 30 weight% nickel and 70 weight% having a thickness of about 0.5 mm was then applied on the interdiffused nickel copper layer by plasma spraying.

 The alloy layer was then pre-oxidised at 1100°C for 6 hours to form a chromium oxide barrier layer on the

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Inconel® structure and a dense hematite-based outer surface layer on the alloy layer.

5 The anode was then tested in molten electrolyte containing approximately 6 weight% alumina at 850°C at a current density of about 0.8 A/cm². The anode was extracted from the cryolite after 100⁴ hours and showed no sign of significant internal or external corrosion after microscopic examination of a cross-section of the anode sample.

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Example 3

15 Example 2 can be repeated by replacing the Inconel® core structure by a nickel-plated copper body which is coated with a chromium layer and oxidised to form a chromium oxide oxygen barrier which can be covered with an interdiffused nickel-copper intermediate layer and the electrochemically active hematite-based outer layer.

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